

Dependence of the Dilatometric Properties of Glasses on Their Structure: I. Borate, Aluminoborate, and Lead-Containing Glasses

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Received March 10, 2005

Abstract—The dependences of the dilatometric properties on the hypothetical structure for a number of borate, aluminoborate, and lead-containing glasses are analyzed over a wide range of compositions. Special attention is focused on the specific features observed in the behavior of the structural temperature coefficient of linear expansion. It is demonstrated that the revealed regularities allow the justified inferences regarding the structural transformations of glasses with variations in their composition.

INTRODUCTION

The dilatometric properties of glasses are considered to mean the temperature coefficients of linear expansion calculated in specified temperature ranges from room temperature to temperatures 10–20 K above the upper limit of the glass transition range, as well as the glass transition temperature T_g measured under standard conditions. The standard conditions of measurements correspond to measurements of dilatometric curves in the course of heating at a rate of 3–4 K/min for samples preliminarily cooled at the same rate from temperatures of the onset of softening. Although the viscosity of glasses at the glass transition temperature is not constant, as was assumed earlier in [1], the glass transition temperature, in our opinion, can be treated as a conventional viscosity characteristic and the viscosity at this temperature is assumed to be close to 10^{12} Pa s (Fig. 1). In this respect, when data on the glass transition temperature are not available, the temperature T_{13} (in degrees Celsius) at which the viscosity of the glass is equal to 10^{12} Pa s will be used instead of the glass transition temperature T_g . The physical meaning of the glass transition temperature and its dependence on the temperature–time conditions of measurements are described in detail in [2].

The structural temperature coefficient of linear expansion α_s became the subject of scientific research only rather recently (see, for example, [3–6]). However, it is evident that this property is extremely important from both the technological [7] and theoretical standpoints [2]. The structural temperature coefficient of linear expansion reflects the change in the specific volume of the glass (and, hence, the relative elongation of the sample under investigation) only due to the temperature changes in the structure under metastable equilibrium conditions, namely, the change in the coordination of

ions, the formation and decomposition of structural fragments (rings, layers, chains), the change in the ratio between the numbers of bridging and nonbridging oxygen atoms, etc. In the present work, an attempt was made to reveal the dependence of the structural temperature coefficient of linear expansion on the structure and to analyze the character of information that can be obtained on structural transformations with a change in the composition of glasses in different glass-forming systems by investigating this property. Moreover, it was of interest to compare the effects of characteristic features of the structure on the structural temperature coefficient of thermal expansion and other dilatometric

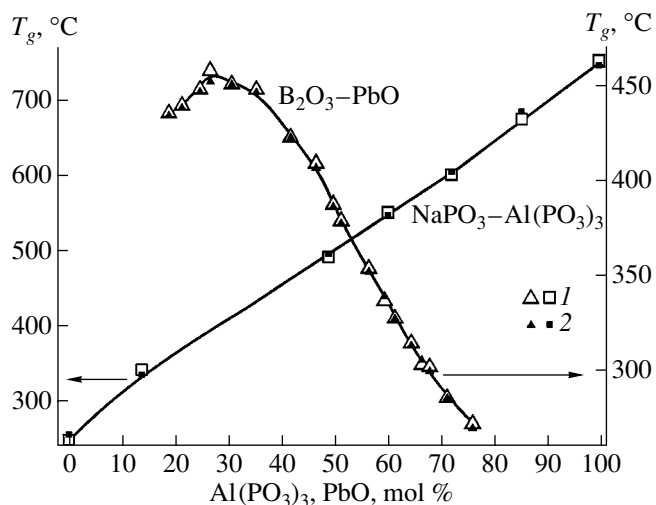


Fig. 1. (1) Glass transition temperatures and (2) isocom T_{13} of glasses in the $\text{NaPO}_3\text{-Al(PO}_3)_3$ and $\text{B}_2\text{O}_3\text{-PbO}$ systems.

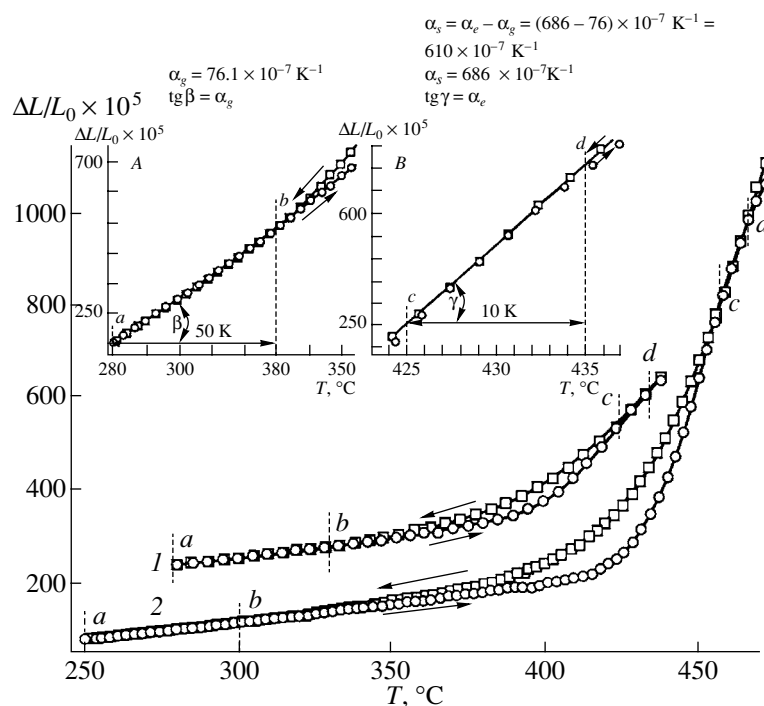


Fig. 2. Dilatometric curves for glasses (1) free from aluminum oxide and (2) containing 9.5 mol % Al_2O_3 at the ratio $\text{Li}_2\text{O}/\text{B}_2\text{O}_3 = 0.18$. Insets show the a - b and c - d portions of curve 1.

properties, such as the temperature coefficient of thermal expansion in the solid state and the glass transition temperature T_g . Recall that the structural temperature coefficient of thermal expansion is the difference between the equilibrium (α_e) and instantaneous (α_g) temperature coefficients of linear expansion: $\alpha_s = \alpha_e - \alpha_g$. Since the accurate determination of the coefficient α_g involves considerable problems, it is expedient to determine this coefficient in a conventionally chosen temperature range below the glass transition range, for example, in the range from T_1 to $(T_1 - 50 \text{ K})$, where T_1 is the lower limit of the glass transition range. The limits of the glass transition range are also conventionally chosen because they are directly related to the dilatometer sensitivity and the reproducibility of experimental results. In our experiments, we assumed that the limits of the glass transition range correspond to the temperatures above and below which the difference between the dilatometric curves obtained upon cooling and heating is no more than 1×10^{-5} . The technique for calculating the temperature coefficients of linear expansion α_e and α_g is illustrated in Fig. 2 [8], which depicts the dilatometric curves for lithium borate and lithium aluminoborate glasses. It can be seen from Fig. 2 that the difference between the temperature coefficients of thermal expansion for two glasses in the temperature range $T_1 - (T_1 - 50 \text{ K})$ is insignificant (it is determined by the difference between the slopes of the corresponding portions of the dilatometric curves). However, the temperature coefficients of thermal expansion at temperatures above the glass transition range differ by a factor of

more than four. This confirms that the structural temperature coefficient of thermal expansion α_g is the specific characteristic of the glass and, in a number of cases, is not related to the thermal expansion of the glass in the solid state.

Note that, in order to obtain sufficiently reliable results in measurements of the thermal expansion above the glass transition range (with a minimum effect associated with the viscous deformations of samples), it is necessary to use a dilatometer with a weak measuring force and samples with a large cross-sectional area, so that the measuring pressure on the sample should not exceed 0.2 N/cm^2 . The technique for the corresponding measurements is thoroughly described in [9].

From analyzing our experimental data with the use of the results of NMR structural investigations [10–13], we made the following assumptions regarding the relation of the structure of glasses to their structural temperature coefficients of linear expansion. (1) The structural temperature coefficient of thermal expansion α_s increases with an increase in the number of nonbridging oxygen atoms in the glass network. (2) The structural temperature coefficient of thermal expansion α_s increases when the glass network contains cations whose coordination numbers change in the temperature range exceeding the lower limit of the glass transition range. (3) The structural temperature coefficient of thermal expansion α_s increases if the glass structure involves chain or layered fragments linked together by weak intermolecular (van der Waals) bonds.

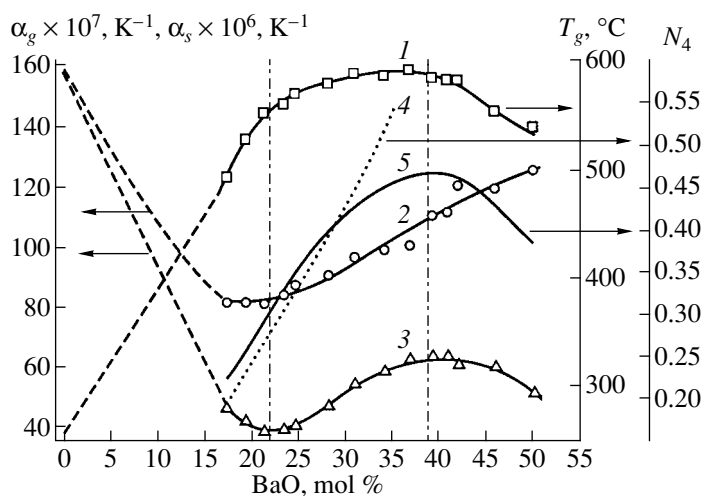


Fig. 3. Dependences of the properties and the fraction of fourfold-coordinated boron on the barium oxide content for glasses in the BaO–B₂O₃ system [14]: (1) T_g , (2) α_g , (3) α_s , (4) N_4 (calculated from the formula in the text), and (5) N_4 ([12], corrected according to [14]). Dashed lines indicate the hypothetical dependences constructed under the assumption that the phase separation is absent in the given composition region.

The above factors are listed in increasing order of their effect on the structural temperature coefficient of thermal expansion α_s . It seems likely that, upon systematic variation in the composition, two factors should predominantly affect the structural temperature coefficient of thermal expansion. In this case, a weakening of the effect of one factor and an enhancement of the effect of another factor should lead to the appearance of extrema in the composition dependences of the structural temperature coefficient of thermal expansion. This situation is observed upon introduction of alkali or alkaline-earth metal oxides into boron oxide. We will analyze the relation of the structural thermal expansion to the structure of borate, silicate, phosphate, and other glasses with a regular variation in their composition. Most attention will be concentrated on the structure of borate and aluminoborate glasses, because it is these glasses that permit one to trace most clearly the effect of all the above three factors on the structural temperature coefficient of thermal expansion. The results obtained in [14–17] will be widely used in our discussion. Note that a large amount of the NMR, IR, and Raman data on the structure of these glasses are available in the literature. However, these data should be analyzed with care because the authors in the study of the same systems sometimes make quite different inferences (see, for example, [18–21]).

RESULTS AND DISCUSSION

Barium Borate Glasses

In order to illustrate the above inferences, let us examine the influence of the composition on the structural temperature coefficient of thermal expansion of barium borate glasses [14]. Furthermore, we also try to reveal the dilatometric properties that are most closely

related to the structural characteristics of glasses. The experimental concentration dependence of the fraction of fourfold-coordinated boron N_4 (constructed from the NMR data and corrected with due regard for an insignificant content of silicon oxide in high-barium glasses [12]) is shown in Fig. 3 (curve 5). The corresponding dependence calculated under the assumption that each BaO molecule introduced into the glass transforms two BO₃ triangles into two BO₄ tetrahedra (this corresponds to the maximum possible content of fourfold-coordinated boron) is depicted by curve 4 in Fig. 3. The calculations were performed from the formula $N_4 = x/(1 - x)$, where x is the mole fraction of BaO oxide. It can be seen from Fig. 3 that, as the BaO content increases to 30 mol %, both dependences differ only slightly (most likely, as a result of errors in the NMR data). However, a further increase in the BaO content leads to an increase in the differences. Note that curve 5 (experimental dependence) lies considerably lower than curve 4. This can be explained by the appearance of BO₃⁻ triangles with nonbridging oxygen atoms in the glass structure. The dependences of the structural temperature coefficient of thermal expansion, instantaneous temperature coefficient of thermal expansion, and the glass transition temperature on the BaO content [14] are also plotted in Fig. 3. The dependence of the structural temperature coefficient of thermal expansion exhibits a minimum in the range 20–25 mol % BaO and a maximum at approximately 40 mol % BaO. As can be seen from Fig. 3, boron oxide is characterized by the maximum values of the structural temperature coefficient and temperature coefficient of linear expansion and the minimum glass transition temperature. This becomes clear taking into account that boron oxide has a layered structure [22]. Layers composed of six-membered boroxol rings, in which boron has a threefold

coordination with respect to oxygen, are joined together only by weak intermolecular bonds. This is responsible for the large values of the structural temperature coefficient and temperature coefficient of linear expansion. Upon introduction of barium oxide, boron transforms into the fourfold coordination. The formed BO_4 tetrahedra, whose negative charge is compensated for by barium ions, link layers of boroxol rings and the layered structure transforms into a three-dimensional structure. This process is accompanied by a decrease in the values of α_s and α_g , because, as was noted above, the layered (or chain) character of the structure has the most strong effect on the temperature coefficient of thermal expansion α_s . The layered structure is most likely responsible for the large temperature coefficients of linear expansion of solid glasses and the low glass transition temperatures. This temperature for pure boron oxide is equal to 258°C. After transforming the layered structure (hypothetically, at 20–25 mol % BaO), the decisive role in the change in the structural temperature coefficient of thermal expansion α_s with a further increase in the BaO content is played by the increase in the content of BO_4 tetrahedra, which at temperatures higher than the lower limit of the glass transition range transform into BO_3^- triangles with an increase in the molar volume [13]. This also favors an increase in the structural temperature coefficient of thermal expansion, even though to a considerably smaller extent (as compared to the layered character of the structure). Such transformations are probably responsible for the minimum in the dependence of the structural temperature coefficient of thermal expansion on the BaO content. A further increase in the BaO content above 30 mol % leads to an increase in the number of BO_3^- triangles with nonbridging oxygen atoms. As a consequence, an increase in the structural temperature coefficient of thermal expansion is retarded and this coefficient passes through a maximum (at approximately 40 mol % BaO) and then decreases. This is attended by a decrease in the content of fourfold-coordinated boron and an increase in the content of threefold-coordinated boron with nonbridging oxygen, which has a weaker effect on the structural temperature coefficient of thermal expansion. Therefore, a complex behavior of the concentration dependence of the structural temperature coefficient of thermal expansion turns out to be closely related to the structural transformations of barium borate glasses. The minimum in the composition dependence of the temperature coefficient of linear expansion α_g in the range 20–25 mol % BaO can be associated with the fact that, at higher BaO contents, repulsive forces between similarly charged boron–oxygen tetrahedra manifest themselves due to the increase in the fraction of fourfold-coordinated boron N_4 . At contents higher than 30 mol % BaO, there appear boron–oxygen triangles with nonbridging oxygen atoms. Both these factors should increase the temperature coefficients of linear expansion of glasses in the

solid state. The same factors most likely govern the behavior of the concentration dependence of the glass transition temperature (Fig. 3, curve 1). The dependences of the fraction of fourfold-coordinated boron N_4 and the structural temperature coefficient of thermal expansion α_s on the composition are similar in shape at BaO contents higher than 30 mol %, and the positions of their maxima at approximately 40 mol % BaO virtually coincide with each other (with a weakly pronounced maximum in curve 1). However, the dependences of the fraction of fourfold-coordinated boron N_4 and the glass transition temperature T_g differ in shape, and the dependence of the temperature coefficient of thermal expansion α_g (curve 2) does not exhibit any features in the range of 40 mol % BaO.

The data on the concentration dependence of the fraction of fourfold-coordinated boron N_4 enable us to estimate the change in the ratio between the structural units (BO_4 tetrahedra, BO_3 and BO_3^- triangles) with a variation in the glass composition. In the above case, we restricted ourselves to qualitative estimates. Note that the results of approximate calculations of percentage of structural units are given in [15–17]. The corresponding calculations will be performed below when considering the structure of lead borate glasses.

In order to compare the dilatometric properties of borate glasses containing lithium, sodium, calcium, and barium oxides, we constructed the dependences of the temperature coefficient of thermal expansion α_g (Fig. 4a), the structural temperature coefficient of thermal expansion α_s , the glass transition temperature (Fig. 4b), and the fraction of fourfold-coordinated boron N_4 (Fig. 4c) on the content of alkali and alkaline-earth oxides. The analysis of these curves demonstrates that the dependences of the temperature coefficient of linear expansion and the structural temperature coefficient of linear expansion for lithium, sodium, and barium borate glasses exhibit minima at oxide contents from 15 to 25 mol %. Note that the minima in the dependences of the temperature coefficient of linear expansion are shifted with respect to those in the dependences of the structural temperature coefficient of linear expansion by 10–15 mol % toward lower contents of modifier oxides. The examination of the positions of the curves with respect to the ordinate axis shows that, in the range of the maximum content of modifier oxides for the pair of alkali oxides and the pair of alkaline-earth oxides, larger structural temperature coefficients of linear expansion correspond to larger fractions of fourfold-coordinated boron N_4 . The maximum fractions of fourfold-coordinated boron N_4 for lithium, sodium, calcium, and barium borate glasses are equal to 0.45, 0.38 [18], 0.54 [13], and 0.47 [12], respectively. As a result, the dependences of the structural temperature coefficient of linear expansion for lithium glasses lie above those for sodium glasses and the corresponding dependences for calcium glasses lie above those for

barium glasses. However, a similar regularity is not observed when comparing alkali glasses with alkaline-earth glasses. Although the fractions of fourfold-coordinated boron N_4 for sodium and calcium glasses differ substantially, their structural temperature coefficients of linear expansion are close to each other (Fig. 4b, curves 2, 3). It seems likely that, apart from the content of fourfold-coordinated boron, the structural temperature coefficient of linear expansion depends substantially on specific features of modifier ions (charge, radius, electron shell). However, the inclusion of this and, possibly, other factors affecting the structural temperature coefficient of linear expansion requires a considerably larger amount of reliable experimental data on the properties and structure of glasses. As could be expected, the effect of the size and charge of modifier cations is traced in the mutual arrangement of the composition dependences of the temperature coefficient of linear expansion and the glass transition temperature T_g . The higher the field strength of the cation (according to Dietzel: z/a^2 , where z is the cation charge, a is the distance between the centers of the cation and oxygen ion [23]), the smaller the temperature coefficient of thermal expansion and the higher the glass transition temperature. General considerations when revealing the dependence of the properties on the hypothetical structure of lithium, sodium, and calcium borate glasses, in principle, are identical to those for the aforementioned barium borate glasses.

Aluminoborate Glasses

In order to analyze in detail the influence of aluminum oxide on the dilatometric properties of glasses, we chose the barium and lithium borate systems, because the structural temperature coefficients of linear expansion are smallest for barium glasses and largest for lithium glasses (Fig. 4b) among all the borate glasses studied to date.

It is known that the introduction of aluminum oxide into glasses containing fourfold-coordinated boron is accompanied by the formation of AlO_4 tetrahedra at the expense of BO_4 tetrahedra [24]. In this case, alkali or alkaline-earth ions compensating for the excess charge of BO_4^- tetrahedra are transferred from boron–oxygen tetrahedra to aluminum–oxygen tetrahedra and the BO_4 tetrahedra transform into BO_3 triangles. When the number of BO_3 triangles (without nonbridging oxygen atoms) is sufficient in the glass structure, an increase in their concentration leads to an increase in the number of boroxol rings, an enhancement of the layered character of the structure, and, hence, an increase in the structural temperature coefficient of thermal expansion. This situation was actually observed in the experiments (Fig. 5). Figure 5a depicts the dependences of the structural temperature coefficient of thermal expansion α_s on the $\text{Al}_2\text{O}_3/\text{BaO}$ ratio at constant $\text{BaO}/\text{B}_2\text{O}_3$ ratios. All the dependences with $\text{BaO}/\text{B}_2\text{O}_3$ ratios from 0.21 to

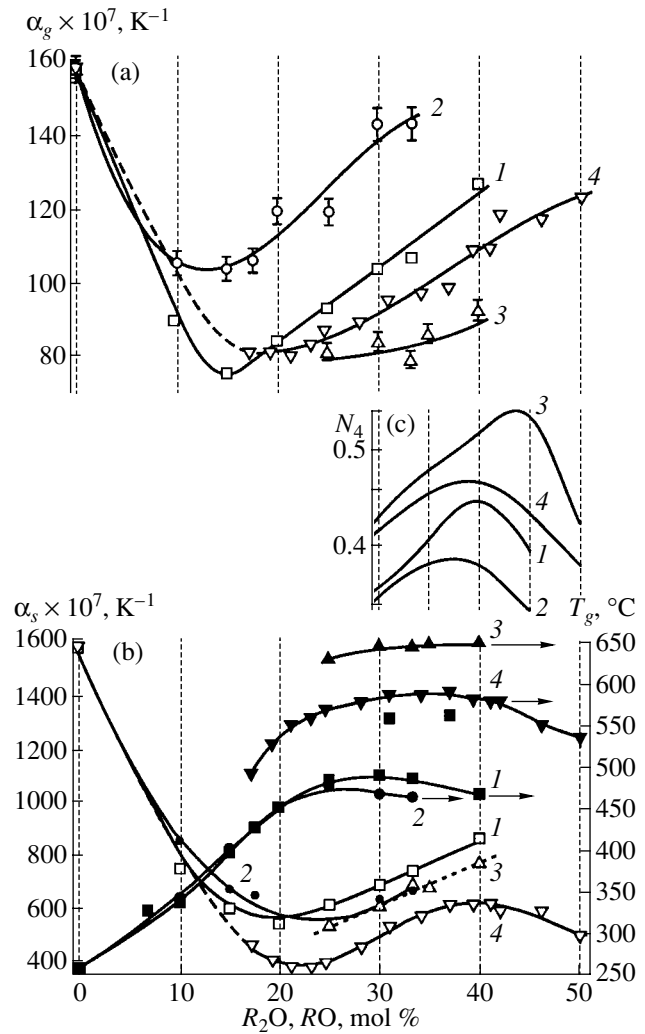


Fig. 4. Dependences of the fraction of fourfold-coordinated boron and the properties on the modifier oxide content for (1) lithium, (2) sodium, (3) calcium, and (4) barium borate glasses.

0.45 are characterized by maxima at $\text{Al}_2\text{O}_3/\text{BaO} = 1-1.2$. Note that the height of the maxima decreases with an increase in the $\text{BaO}/\text{B}_2\text{O}_3$ ratio and the maxima in this range disappear at $\text{BaO}/\text{B}_2\text{O}_3 > 0.45$. A similar behavior is observed for the dependences of the structural temperature coefficient of thermal expansion for lithium glasses. However, the structural temperature coefficients of linear expansion for these glasses are considerably larger than those for the barium glasses (Fig. 5b). The maximum structural temperature coefficient of linear expansion for the barium glass (at $\text{BaO}/\text{B}_2\text{O}_3 = 0.21$) is equal to $1140 \times 10^{-7} \text{ K}^{-1}$, whereas this coefficient for the lithium glass (at $\text{Li}_2\text{O}/\text{B}_2\text{O}_3 = 0.18$) is $2120 \times 10^{-7} \text{ K}^{-1}$, i.e., is nearly two times larger. It is of interest that this coefficient even exceeds the structural temperature coefficient of linear expansion for pure vitreous boron oxide ($1590 \times 10^{-7} \text{ K}^{-1}$), for which the lay-

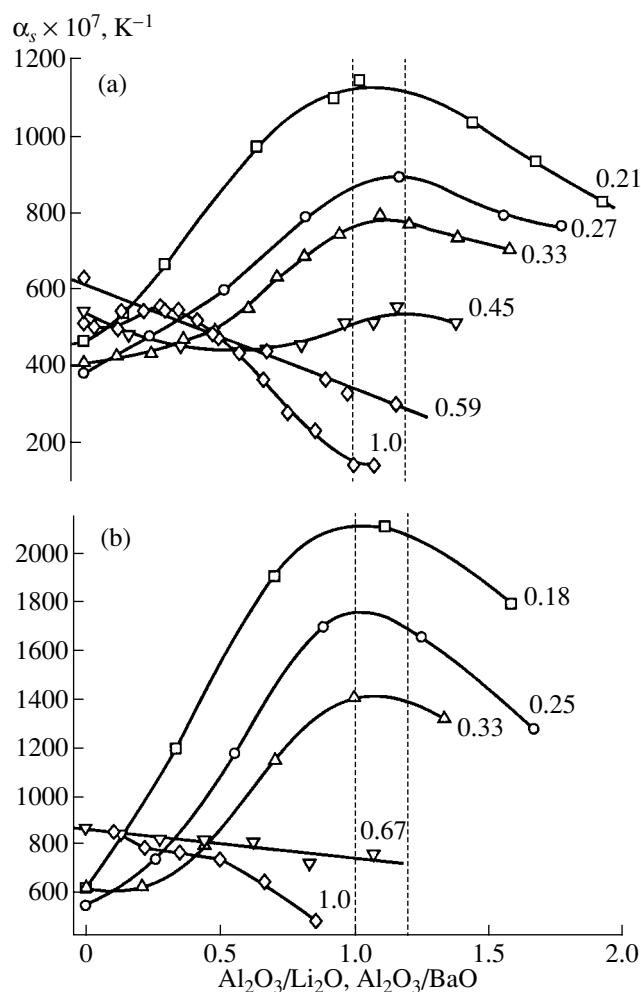


Fig. 5. Dependences of the structural temperature coefficient of thermal expansion on the $Al_2O_3/Li_2O(BaO)$ ratio for (a) barium and (b) lithium borate glasses. Numbers near curves indicate the $Li_2O(BaO)/B_2O_3$ ratios.

ered structure seemingly should have the strongest effect. It is obvious that, in order to offer a more or less justified explanation for these differences, it is necessary to carry out additional investigation into the structure of lithium aluminoborate glasses.

It seems likely that, as the aluminum oxide content increases, almost all boron atoms at a ratio Al_2O_3/R_2O ($RO \approx 1$) appear to be in the threefold-coordinated state and a further increase in the number of AlO_4 tetrahedra becomes impossible. As a consequence, a further increase in the Al_2O_3 content results in the formation of sixfold-coordinated aluminum, which plays the role of a modifier rather than a network former. In this case, the glass network contains an increasing number of BO_3 triangles with nonbridging oxygen atoms, which, as was noted above, make a considerably smaller contribution to an increase in the structural temperature coefficient of thermal expansion. Therefore, an increase in the aluminum oxide content above the content corre-

sponding to the ratio $R_2O(RO)/Al_2O_3 \approx 1$ leads to a decrease in the structural temperature coefficient of thermal expansion (Fig. 5). This is probably responsible for the appearance of the maxima in the dependences of the structural temperature coefficient of thermal expansion. A decrease in the height of the maxima with an increase in the BaO or Li_2O content is most likely associated with the corresponding decrease in the boron oxide content in glasses, in the concentration of threefold-coordinated boron atoms (BO_3 triangles without nonbridging oxygen atoms), and, hence, in the number of boroxol rings and layered structural fragments formed by these rings.

The largest structural temperature coefficients of linear expansion are characteristic of lithium aluminoborate glasses. It seems likely that the nature of the cation compensating for the negative charge of the aluminum–oxygen tetrahedron is of crucial importance in this case. However, reliable data on structural transformations accompanying the incorporation of aluminum–oxygen tetrahedra into the network of borate glasses are not available in the literature. It should be noted that the effect of the layered structure manifests itself only in the case when the content of BO_3 triangles becomes higher than 65–70 structural percent [18]. (The structural percent is considered to mean the percentage of particular structural units with respect to the sum of all structural units, such as BO_3 , BO_4 , AlO_4 , etc., that form the glass network.) As a result, the introduction of aluminum oxide into the glasses with the maximum content of modifier oxides, in which the content of BO_3 boron–oxygen triangles with bridging oxygen atoms is insignificant, results in a decrease in the structural temperature coefficient of thermal expansion, as can be seen from Fig. 5.

Now, we attempt to reveal extrema in the composition dependences of the glass transition temperature and to relate them to the hypothetical structural features. The dependences of the glass transition temperature on the BaO/B_2O_3 ratio for barium glasses and on the Li_2O/B_2O_3 ratio for lithium glasses are depicted in Fig. 6. The dependence at the ratio $BaO/B_2O_3 = 0.21$ exhibits an almost linear behavior. The other dependences are characterized by the minima, which are most pronounced at BaO/B_2O_3 ratios of 0.39 and 0.59 (Fig. 6a). A similar behavior is observed for lithium glasses, for which the minima of the glass transition temperature are found in the curves at Li_2O/B_2O_3 ratios of 0.50 and 0.67 (Fig. 6b). Note that, for barium and lithium glasses, the positions of the minima with respect to the abscissa axis are observed at Al_2O_3/Li_2O (BaO) ratios in the range from 0.5 to 0.7. However, the dependences of the glass transition temperature T_g do not exhibit any features at ratios close to unity, i.e., in the range in which maxima occur in the dependences of the structural temperature coefficient of thermal expansion. As regards the nature of the minima in the depen-

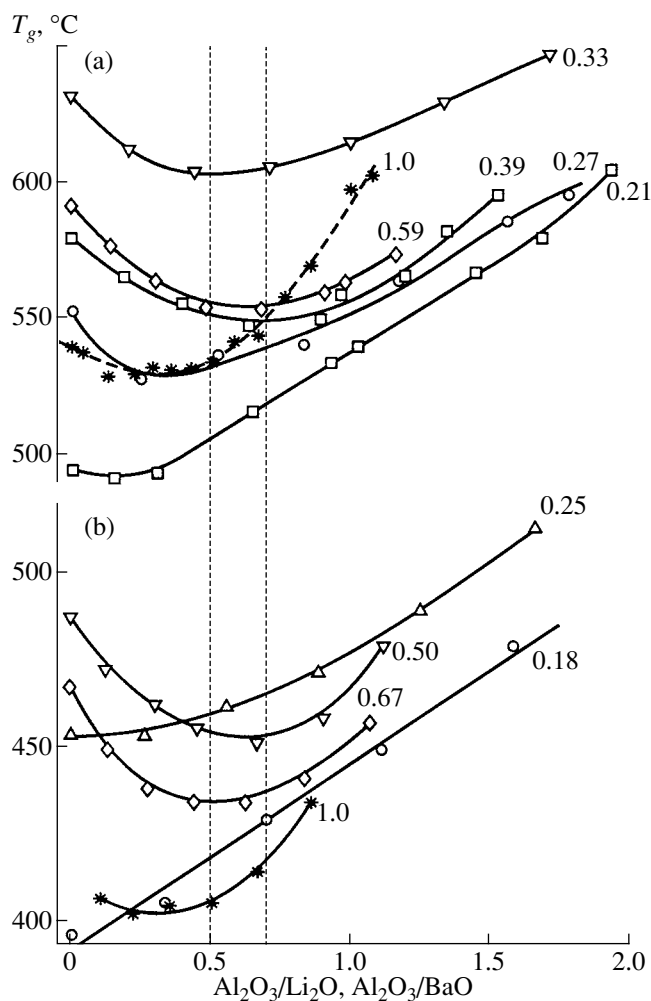


Fig. 6. Dependences of the glass transition temperature T_g on the $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}(\text{BaO})$ ratio for (a) barium and (b) lithium borate glasses. Numbers near curves indicate the $\text{Li}_2\text{O}(\text{BaO})/\text{B}_2\text{O}_3$ ratios.

dependences of the glass transition temperature T_g , we can only assume that the introduction of aluminum oxide is accompanied by two processes of structural transformations that lead to opposite effects, namely, to a weakening of the structure due to the increase in the content of BO_3 triangles and a strengthening of the structure by AlO_4 tetrahedra. It is possible that some glass properties are predominantly affected by the former process upon addition of the first portions of aluminum oxide and by the latter process upon introduction of subsequent portions [14].

The influence of aluminum oxide on the properties (and, most likely, on the structure) of sodium and calcium borate glasses is not characterized by specific features. Figure 7 depicts the dependences of the structural temperature coefficient of thermal expansion and the glass transition temperature on the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$, $\text{Al}_2\text{O}_3/\text{CaO}$, and $\text{Al}_2\text{O}_3/\text{BaO}$ (for comparison) ratios at

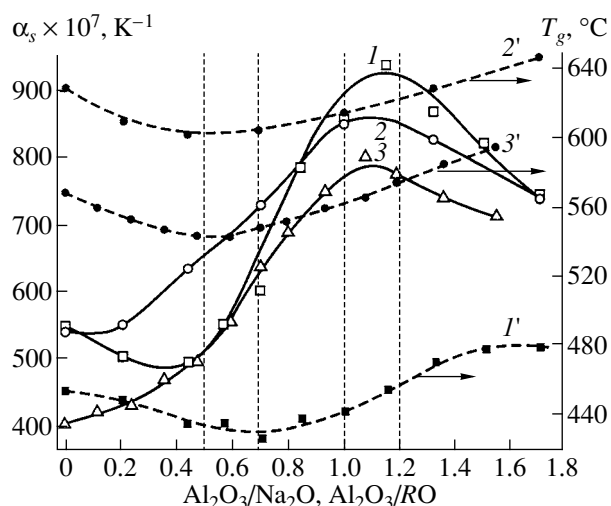


Fig. 7. Dependences of (1–3) the structural temperature coefficient of thermal expansion and (1'–3') the glass transition temperature T_g on the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{Al}_2\text{O}_3/\text{RO}$ ratios at the ratios $\text{Na}_2\text{O}(\text{RO})/\text{B}_2\text{O}_3 = 0.33$ for (1, 1') sodium, (2, 2') calcium, and (3, 3') barium glasses.

the ratio $\text{Na}_2\text{O}(\text{RO})/\text{B}_2\text{O}_3 = 0.33$ identical for all glasses. It can be seen from Fig. 7 that the dependences of the structural temperature coefficient of thermal expansion exhibit minima at ratios of 1.1 and the dependences of the glass transition temperature are characterized by minima at ratios in the range from 0.5 to 0.7. The largest and smallest structural temperature coefficients of linear expansion at the maximum are observed for sodium and barium glasses, respectively. The glass transition temperatures increase in accord with an increase in the field strength of the modifier cation [23]: $T_g(\text{Na}) < T_g(\text{Ba}) < T_g(\text{Ca})$.

No extrema are found in the dependences of the temperature coefficient of thermal expansion α_g for solid glasses in the systems under consideration (Fig. 8).

Thus, we considered the basic approaches to revealing the relation of the dilatometric properties to the hypothetical structure of borate and aluminoborate glasses. Now, we attempt to determine the applicability of the established regularities to systems containing other glass-former oxides.

Lead Borate, Lead Silicate, and Lead Germanate Glasses

As is known, the borate, silicate, and germanate systems with lead oxide have a very wide glass formation regions and the lead oxide content can considerably exceed 50 mol %. Let us initially analyze lead borate glasses. It is universally accepted that, as the lead oxide content increases, lead oxide begins to play the role of a network former oxide. In this case, lead forms lead–oxygen structural units, in which lead atoms occupy vertices of polyhedra, i.e., tetragonal [11] or trigonal

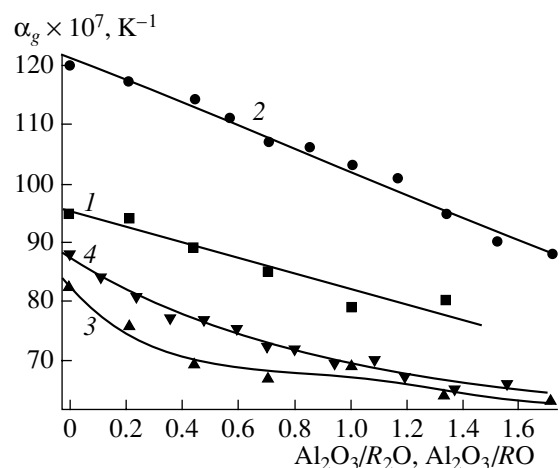


Fig. 8. Dependences of the instantaneous temperature coefficient of thermal expansion on the Al_2O_3/R_2O and Al_2O_3/RO ratios for (1) lithium, (2) sodium, (3) calcium, and (4) barium glasses.

[25] pyramids. It is of interest to reveal how this circumstance reflects in the dilatometric properties of glasses. Figure 9 depicts the concentration dependences of the structural temperature coefficient of thermal expansion, the instantaneous temperature coefficient of thermal expansion, the glass transition temperature [3], the fraction of fourfold-coordinated boron [11], and the fraction of the maximum content of fourfold-coordinated boron in the case when each PbO molecule transforms two boron atoms from the threefold-coordinated state into the fourfold-coordinated state. By comparing the dilatometric properties of barium borate (Fig. 3) and lead borate (Fig. 9) glasses, it is easy to see that, for lead borate glasses, the maximum in the

dependence of the glass transition temperature coincides with the minimum in the dependence of the structural temperature coefficient of thermal expansion at a PbO content of 26–28 mol %. Moreover, the maxima in the dependences of the fraction of fourfold-coordinated boron N_4 and the structural temperature coefficient of thermal expansion at 48–50 mol % PbO coincide with each other. The positions of the minima in the dependences of the structural temperature coefficient of thermal expansion and temperature coefficient of thermal expansion α_g with respect to the composition axis for barium and lead glasses are close to each other. However, the maxima in the dependences of the fraction of fourfold-coordinated boron N_4 and the structural temperature coefficient of thermal expansion for lead glasses are shifted as compared to those for barium glasses by approximately 10 mol % toward higher PbO contents. The reason for this shift becomes clear by assuming that only a part of lead ions (proportional to the number of fourfold-coordinated boron atoms) participate in the neutralization of excess charges of BO_4^- tetrahedra and the other lead ions in the form of lead-oxygen polyhedra are incorporated into the glass network. In this case, it is possible to calculate the number of structural units (BO_3, BO_4, PbO_n) involved in the formation of the glass network under the assumption that $|PbO_n| = |Pb| - |Pb_i|$, where $|Pb|$ is the total content of lead atoms introduced into the glass and $|Pb_i|$ is the content of lead atoms participating in the neutralization of negative charges of BO_4^- tetrahedra. Note that one lead ion neutralizes the excess charge of two boron-oxygen tetrahedra. The calculated dependences of the percentage of structural units on the PbO content in the range from 26 to 76 mol % are plotted in Fig. 10. Most likely, beginning with 26–28 mol % PbO, the number of BO_3

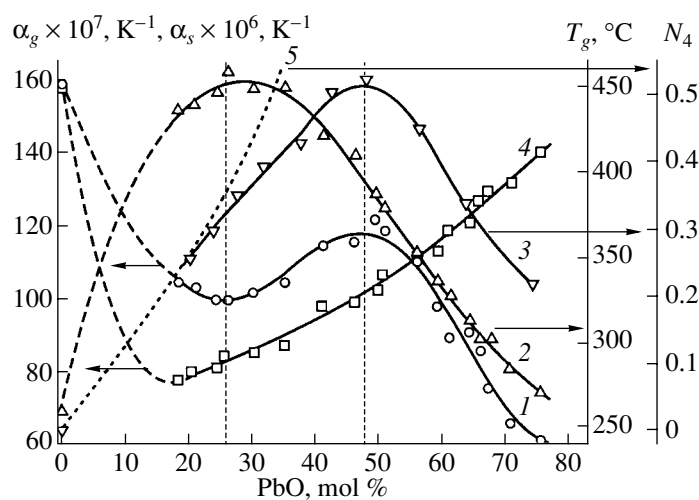


Fig. 9. Dependences of (1) the structural temperature coefficient of thermal expansion α_s , (2) the glass transition temperature T_g , (3) the fraction of fourfold-coordinated boron N_4 [11], (4) the temperature coefficient of thermal expansion α_g , and (5) the fraction N_4 (calculated from the formula in the text) on the PbO content for lead borate glasses. Dashed lines indicate hypothetical dependences constructed under the assumption that the phase separation is absent in the given composition region.

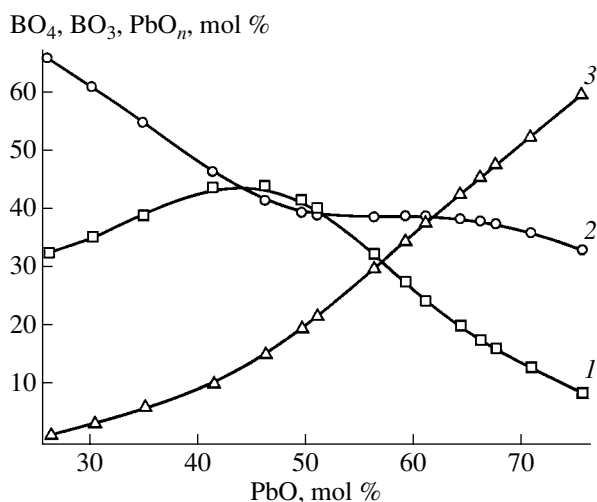


Fig. 10. Dependences of the percentage of structural units on the PbO content for lead borate glasses: (1) boron–oxygen tetrahedra, (2) boron–oxygen triangles, and (3) lead–oxygen polyhedra.

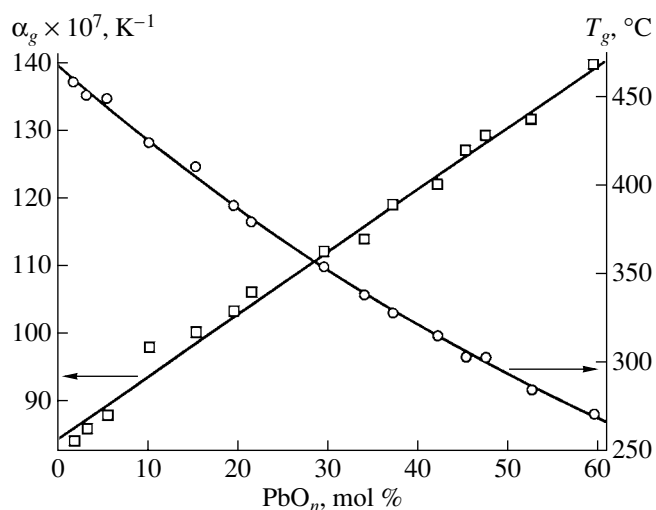


Fig. 11. Dependences of the temperature coefficient of thermal expansion α_g and the glass transition temperature T_g on the percentage of lead–oxygen polyhedra in the structure of lead borate glasses (see Fig. 10).

triangles and, hence, the number of boroxol rings decrease so that the layered character of the structure does not substantially affect the dilatometric properties of glasses. The role of weakened structural regions is played by Pb–O ionic–covalent bonds in lead–oxygen polyhedra. This is confirmed by the dependences shown in Fig. 11, according to which the glass transition temperature can decrease and the instantaneous temperature coefficient of thermal expansion can increase depending on the percentage of lead–oxygen structural units (see Fig. 10). The glass transition temperatures T_g fit well a quadratic dependence with a small curvature, and the instantaneous temperature coefficient of thermal expansion α_g is adequately described by a linear dependence.

The dependences of the dilatometric properties on the lead oxide content for lead silicate [11], lead germanate, and lead borate glasses are compared in Fig. 12. The dependences of the instantaneous temperature coefficient of thermal expansion do not exhibit pronounced extrema. The exception is provided by the minimum at approximately 20 mol % PbO in the curve for borate glasses. This minimum is probably governed by the transformation of the layered structure into the three-dimensional structure and by the appearance of lead–oxygen tetrahedra with a subsequent increase in the PbO content (see Figs. 10, 11). In the range of low PbO contents, the smallest values of the temperature coefficient of thermal expansion are observed for silicate glasses (due to the large number of firmly linked silicon–oxygen tetrahedra). However, an increase in the PbO content results in a decrease in the differences between the positions of the dependences for silicate, germanate, and borate glasses and the differences become insignificant at 50 mol % PbO. A further increase in the PbO content leads to the disappearance

of differences between the curves for silicate and borate glasses, because their thermal expansion is completely determined by the lead–oxygen polyhedra. In the range 20–50 mol % PbO, the temperature coefficients of linear expansion α_g for germanate glasses are somewhat larger than those for borate glasses, even though the temperature coefficient of thermal expansion for vitreous germanium dioxide is nearly half as much as that for vitreous boron oxide. This is explained by the difference between the structures of vitreous boron oxide (layered structure) and vitreous germanium dioxide (three-dimensional structure formed by GeO_4 tetrahedra).

The composition dependence of the temperature T_{13} for lead borate glasses (Fig. 12) virtually coincides with that for the glass transition temperature T_g (see Fig. 1). The corresponding dependence for lead silicate glasses is governed by the presence of silicon–oxygen tetrahedra in the structure and, hence, lies above the dependence for lead borate glasses.

The composition dependence of the temperature T_{13} for lead germanate glasses exhibits a specific behavior. In the range 10–30 mol % PbO, the temperature T_{13} depends only slightly on the composition (this was previously noted by Nemilov [26]), most likely, due to the transformation of germanium atoms from the fourfold-coordination state into the sixfold-coordinated state with respect to oxygen. Ivanov and Evstrop'ev [27] studied the physical properties of lead germanate glasses and made the inference that the content of sixfold-coordinated germanium increases with an increase in the PbO content from 0 to 30 mol %. The composition dependence of the structural temperature coefficient of thermal expansion exhibits a pronounced maximum at approximately 25 mol % PbO (Fig. 12). We can assume that this PbO content corresponds to the

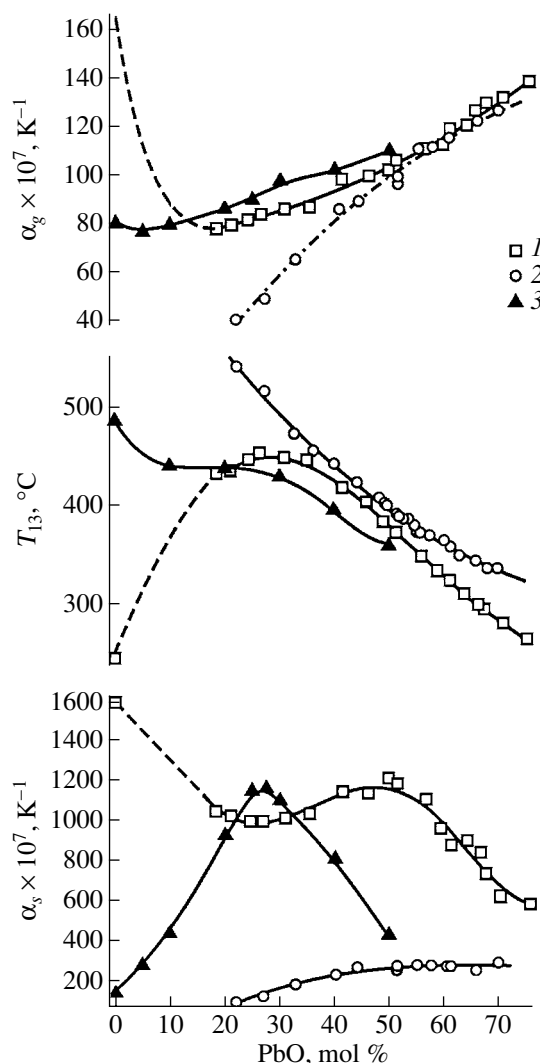


Fig. 12. Dependences of the temperature coefficient of thermal expansion α_g , the temperature T_{13} , and the structural temperature coefficient of thermal expansion α_s on the PbO content for (1) lead borate, (2) lead silicate, and (3) lead germanate glasses.

maximum content of sixfold-coordinated germanium. The smallest structural temperature coefficients of linear expansion are observed for lead silicate glasses. However, it should be noted that the extrapolation of the dependences of the structural temperature coefficient of linear expansion for lead borate and lead silicate glasses to 100 mol % PbO indicates that their structural temperature coefficients of linear expansion nearly coincide with each other [28].

CONCLUSIONS

Thus, the comparison of the dilatometric properties and the hypothetical structure of the glasses under consideration allowed us to make the inference that the temperature coefficient of linear expansion α_g for

glasses in the solid state provides the least amount of information on features of structural transformations in glasses with a variation in the composition and, in a number of cases, reflects only the transformation from a layered structure into a three-dimensionally linked structure. Moreover, it was revealed that there is a correlation between the temperature coefficient of linear expansion and the field strength of the modifier cation.

The glass transition temperatures characterize the mean strength of the glass structure. The concentration dependences of the glass transition temperature (or T_{13}) permit one to evaluate the change in the strength of bonds between structural units involved in the formation of the glass network.

The structural temperature coefficient of linear expansion drastically increases in the case when the glass structure becomes layered and varies to a smaller extent when structural units whose coordination with respect to oxygen is changed with a change in the temperature are formed in the glass network. As a rule, there is a good correlation between the content of these units and the structural temperature coefficient of linear expansion.

A combined analysis of all the three aforementioned dilatometric properties of glasses provides the largest amount of structural information. However, valuable data on the structural features can be obtained using only the structural temperature coefficients of linear expansion and the glass transition temperatures.

Further investigations into the relation of the dilatometric properties to the structure of glasses should be associated with improving the quality of measurements, revealing the general principles for calculating the dependence of the properties on the content of particular structural units, and extending the range of glass-forming systems. It is especially desirable to elucidate the factors responsible for the unusually large structural temperature coefficients of linear expansion for lithium aluminoborate glasses.

ACKNOWLEDGMENTS

The author would like to thank B.Z. Pevzner for careful reading of the manuscript and for a number of valuable remarks made in the discussion of the results obtained in this study.

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